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HILDEBRAND (71) We, ROBERT HILDEBRAND MASCHINENBAU GmbH. Nurtinger Strasse, 68, D7466 Oberboihinger, Germany, a German Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

The present invention relates to a method and apparatus for curing and hardening a coating which is applied upon a base or other support and consists of an organic material which when energized by being 15 exposed to at least one flash of ultraviolet rays reacts exothermically. When speaking herein of a material which reacts exothermically, a material is meant which gives off

energy during its reaction, for example, a 20 varnish which dries by oxidation and may especially be either a synthetic resin var-nish or an oil varnish.

In one prior method for curing a film consisting of an unsaturated polyester, a 25 photosensitizer is added to this material. By being exposed to flashes of ultraviolet light of at least 50 west appearance. light of at least 50 watt seconds per flash and at photochemically active-wave lengths, these photosensitizers release radicals which initiate the reaction in the polyester film. Since the quantity of photosensitizers which is added to the polyester amounts to 0.5% of the latter, a reaction will occur at first only in up to 5% of the outer surface area 35 of the polyester film. It is therefore necessary to carry out a very large number of flashes in order to attain the desired final cure of the film. In order to reduce the length of time which is required for the 40 entire curing process, a plurality of flash tubes are provided which produce flashes successively. The amount of ultraviolet successively. The amount of ultraviolet light which is required for fully curing the polyester film may be reduced if the base to 45 be coated with this film is first primed with

[Price 25p]

a ground coating upon which the polyester film is then applied, whereupon this primed and coated base is then subjected to a heat treatment before it is exposed to the ultraviolet rays.

(11)

According to one aspect of the present invention, there is provided a method of curing and hardening a coating applied in a liquid condition upon a base and consisting of an organic material not containing a 55 photosensitizer which reacts exothermically including the step of energizing the organic material by exposing it to at least one flash of ultraviolet rays which directly initiates the reaction in said material, said ultraviolet rays comprising at least a component having a wave length equal to 197.4 nm effective for curing said material and lying within the resonant range of a radical of the material of said coating to be cured.

If a flash of ultraviolet light acts directly upon the material, the reaction of the coating which is exposed to this light will start along its entire surface and will penetrate from the latter to the inside of the coating 70 like a chain reaction, whereby the organic, exothermically reacting material will be cured and hardened within a very short time. Thus, for example, a single short flash of ultraviolet rays may suffice for curing and 75 hardening such an organic, exothermically

reacting material.

According to another aspect of the present invention there is provided an apparatus for carrying out the process claimed 80 in claim 1 comprising means for applying a coating to a base, an ignition unit and a flash lamp connected to said ignition unit and adapted to produce a flash of ultraviolet rays in order directly to initiate the reac-tion of said material said flash lamp being adapted to produce flashes of ultraviolet rays, having a component of a wave length equal to 197.4 nm effective for curing said material and lying within the resonant range 98

of the radical of said material to be cured. The component of effective wave length does not have to amount to a large component of the entire wave range of the rays of each flash but only a small component of this range will suffice which lies within the resonant range of the radical of the material to be cured. However, the larger this component is made, the shorter will be the 10 length of time which is required for fully curing and hardening the material. If the wave range of each flash is sufficiently large, it may also be of advantage to employ additional wave lengths of 184.9 and/or 15 389.0 nm.

For curing and hardening a coating of an organic material which is applied upon a base and after being energized by being exposed to ultraviolet rays reacts exothermically, the invention further provides an apparatus which comprises an ignition unit and a flash lamp connected to the ignition unit and adapted to produce a flash of ultraviolet rays in order directly to initiate the reaction of said material without previously requiring the addition of photosensitizers thereto so as to cure and harden the material.

The invention will now be described, by 30 way of example only, with reference to the accompanying drawings, in which— Figure 1 shows a diagrammatic cross

Figure 1 shows a diagrammatic cross section of an apparatus according to the invention;
Figure 2 shows a graphic illustration of

35 Figure 2 shows a graphic illustration of flash impulses which are produced by an ultraviolet lamp which is connected to a source of alternating current;

source of alternating current;
Figure 3 shows a diagrammatic graphic to illustration of flash impulses of the flash lamp of the apparatus according to the invention; while

Figure 4 shows a circuit diagram of an

ignition unit of this apparatus.

The apparatus according to the invention as illustrated in Figure 1 comprises a housing 1 which is closed toward the outside and contains a conveying mechanism 2, for example, in the form of rollers which are

example, in the form of rollers which are 50 driven from the outside and are adapted to convey, for example, relatively thin flat elements 3 which are provided with a coating 4 consisting of a synthetic resin varnish or oil varnish which is capable of drying by 55 oxidation. On the upper wall of housing 1

a flash tube 5 is mounted which is connected to an ignition unit 6 and produces flashes of ultraviolet rays at least a certain component of which has a certain wave

60 length or frequency.

If the flash tube 5 would be connected to a conventional source of alternating current, it would emit flash impulses of the kind as illustrated in Figure 2. However, 65 by being connected to the ignition unit 6,

tube 5 will produce flash impulses of a shape as illustrated in Figure 3 or of amother shape similar thereto. Depending upon the kind of flash tube employed, it may be necessary to supply it with a base voltage of a certain minimum strength. Such a base voltage is not required if the flash tube consists, for example, of a xenon-filled tube which is provided with an additional ignition winding and the sealed bulb of which 75 preferably consists of a quartz or the like which is highly permeable for the desired wave length. If, however, a mercury-vapor lamp is employed, it has to be supplied with a base voltage for preventing it from 80 being extinguished after each flash.

As illustrated in Figure 4, the ignition unit 6 for tube 5 is provided with a transformer 7 which is to be connected to a

former 7 which is to be connected to a source of alternating current and the secondary side of which is connected via a oneway rectifier 8 and a resistor 9 to the electrodes of tube 5 which is also connected in parallel to a condenser 10. An ignition circuit which is likewise connected to the 90 secondary side of the transformer 7 comprises a two-way rectifier 11, 12 in a bridge circuit which contains a smoothing condenser 13 one side of which is connected to one of the electrodes of tube 5, while its 95 other side together with the rectifier 11, 12 is connected via a resistor 14 to a hightension or ignition transformer 16 to which an ignition condenser 15 and a switch 17 are connected in parallel. This switch 17 100 may be a pulse switch, a thyristor or the like. The ignition transformer 16 is connected to an ignition winding 18 of tube 5. The ignition unit 6 is adapted to produce short flashes as illustrated in Figure 3, each 105 of which lasts for about one thousandth of a second\_and\_which\_are\_separated\_from\_each other by long intervals. The longer the intervals are made between the individual flash impulses which may also be of a shape 110 different from that as shown in Figure 3, the smaller will be the amount of energy which is required for curing and hardening the coating material.

As previously described, the apparatus 115 according to the invention is to be used for curing and hardening a coating which is applied upon a base or support and consists of an organic material which when energized by being exposed to radiation 120 reacts exothermically and continues to react when the flash is completed. This material especially comprises a varnish which dries by oxidation. This may be, for example, a synthetic resin varnish or an 125 oil varnish. These kinds of varnishes are relatively inexpensive and are therefore more frequently employed in industry than other varnishes.

When a flash of light from tube 5 hits 130

3

upon the surface of the coating, it starts a reaction in the latter and continues in the form of a chain reaction into the inside of the coating. This reaction is very intensive 5 since a large number of molecules of the surface layer participate therein. Under favorable conditions a single flash may suf-Under fice for curing and hardening the coating, while in other cases several flashes will be

10 required. When the varnishes employed are being cured, an energy-producing or exothermic reaction occurs therein which is caused or initiated by at least one flash of a certain 15 wave length. As already stated, the varnishes continue to react to a certain extent when the respective flash is completed. When this organic material is exposed to a flash, the radical of this material is ener-

20 gized at a frequency which corresponds to its inherent frequency, and this radical participates in the curing process of the material, for example, a varnish drying by pridetion, whereby overen a 20tivated. oxidation, whereby oxygen is activated. For 25 the greatest effect the rays must have a frequency which corresponds to the resonant frequency of the radical of the coating which combine with oxygen. In all varnishes

to which the method according to the inven-30 tion applies, this frequency corresponds to a wave length of 197.4 nm. The curing process may be further accelerated if a small component of the rays has a wave length which corresponds to one of the 35 resonance lines of the oxygen and amounts.

for example, to 184.9. It has also been

found that the curing process may be accelerated if a component of the rays has a

wave length of 389.0 nm.

The number of flash impulses which are to be produced within a certain time unit may differ in accordance with the particular kind of varnish employed, and while in one case a single flash impulse may suffice, it 45 may be necessary in other cases to apply 10 to 20 flash impulses per second. The number of flash impulses which have to impinge upon the coating for curing and hardening the same depends upon the type 50 of material and the thickness of the casing of the flash tube and upon the component of effective rays of all of the rays emanating from the tube, and also upon the thickness of the coating, the permeability of the 55 coating to the penetration of the rays ap-

plied and upon similar factors. The energy-producing or exothermic reaction of the coating materials employed must be initiated by flash impulses of a 60 certain frequency and must continue at least for a certain length of time after each flash is terminated. For reducing the length of the period required for the curing process the varnishes to be dried may be fixed with

65 quickly evaporating solvents of a low boil-

ing point, for example, with ethyl acetate, butanol, acetone or the like. The addition of chromic acid or of ammonium bichromate from which chromic acid is formed at the moment of a flash has an additional 70 curing and hardening effect.

The energy of the rays which is required

for the curing process is the lower the longer the interval between the flash impulses is made as compared with the length of time of 75 one flash. Thus, it has been found that when this relation is made of a value of 100:1, very good curing and drying results will be attained at an extremely low output

of power.

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A wave length which has proved effective for curing a preferred exothermically reacting organic material has been found to be the length of 197.4 nm which is the resonant frequency of the radical of the material to be cured. The short-wave component in which the wave length of 197.4 nm occurs in an ultraviolet lamp may be increased by employing a current of a density of more than 4000 A/cm<sup>2</sup> for producing one flash 90 at an output of less than 100 watt seconds and by making the length of the flash smaller than 50 microseconds. The higher the current density is made, the larger will be the short-wave component containing the 95 wave length of 197.4 nm and the current density may be made much higher than the value as previously stated and may amount to about 30 000 A/cm<sup>2</sup>.

If the flashes only last for a short time, 100 the electrodes of the flash tube will not be highly heated and it will therefore be necessary to cool them very little, if at all. A favorable length of the flashes lies within the range of 20 to 30 milliseconds. If each 105 flash has a shorter length, the frequency of the flashes may be made much higher than that which is possible if the flashes last for longer periods, and they may amount, for example, to 100 flashes per second and 110 more. At a higher frequency, the number of flashes within a certain time unit and thus also the effective wave-length component of the entire wave range will be higher than at a lower frequency. This component may 115 therefore be considerably increased when the frequency of the flashes is increased. At short flashes, the amount of energy emitted from each flash and received by the coating will also be low.

The required power output of each flash amounts to less than 100 watt seconds and in actual practice it generally amounts to a much lower value and lies, for example, within an order of about 20 watt seconds. 125

For drying a coating material which consists of a synthetic-resin varnish or oil varnish and dries by oxidation, a xenon flash tube is preferably employed. The frequency of the flashes of such a tube amounts to 130

10 cycles per second and the flash output to slightly less than 100 watt seconds at an anode voltage of 4 KV. The following examples were carried but with such a 5 flash tube for curing at 1 hardening particular coating materials is accordance with the invention:

1. A varnish consisting of 35% of styrolized alkyd, 50% titanium dioxide and 15% of a solvent, for example, high-grade gasoline, and with the thickness of the coating amounting to 30 micrometers was fully cured and hardened after being exposed to

400 flashes.

2. A mixture of 60% of aluminum-reinforced soy oil, 30% of iron oxide red, and 10% of xylol with a thickness of the coating of 30 micrometers was fully cured and hardened after being expose i to 300 20 flashes.

3. A colorless varnish consisting of 68% of vegetable fatty acids and 32% of a solvent, for example, high-grade gasoline, and with a thickness of the coating of 25 25 micrometers was fully cured and hardened

after being exposed to 600 flashes.

4. A printing ink of a commercial type which consisted of a material which dries by oxidation and contained no addition of 30 siccatives and had a layer thickness of about 3 micrometers was applied by a print ing press upon paper. The ink was com-pletely dried and cured after being exposed

to 10 flashes.

The invention therefore relates to the curing and hardening of a coating which is applied in a liquid condition upon a base and consists of an organic material which reacts exothermically when energized by being exposed to one or more flashes of ultraviolet rays of a flash lamp which directly initiate the reaction in the coating material without requiring photosensitizers to be

added to this material. Although my invention has been illustrated and described with reference to the preferred embodiments thereof, I wish to have it understood that it is no way limited to the details of such embodiments but is

50 capable of numerous modifications within the scope of the appended claims.

WHAT WE CLAIM IS:-

1. A method of curing and hardening 55 a coating applied in a liquid condition upon a base and consisting of an organic material not containing a photosensitizer which reacts exothermically including the step of energizing the organic material by exposing it 60 to at least one flash of ultraviolet rays which directly initiates the reaction in said material, said ultraviolet rays comprising at least a component having a wave length equal to 197.4 nm effective for curing said material 65 and lying within the resonant range of a

radical of the material of said coating to be

A method as defined in Claim 1, in which said rays have an additional component with an effective wave length of 184.9 70

A method as defined in Claim 1 or 2, in which said rays have an additional component with an effective wave length of 389.0 nm.

A method as defined in claim 1, in which said coating is exposed periodically to a plurality of flashes all lasting for a substantially equal length of time and each being separated from the next flash for a 80 period of time having a length equal to a large multiple of the length of time of one of said flashes.

5. A method as defined in claim 4, in which each of said periods of time between 85 successive flashes is more than one hundred times as long as the length of time of one

of said flashes.

6. A method as defined in claim 1, in which for producing said flash a flash lamp 90 is employed and supplied with a current having a density of more than 4000 A/cm² and an ouput of less than 100 watt seconds, said flash lasting for a period of less than 50 microseconds.

An apparatus for carrying out the process claimed in claim 1 comprising means for applying a coating to a base, an ignition unit and a flash lamp connected to said ignition unit and adapted to produce a 100 flash of ultraviolet rays in order directly to initiate the reaction of said material said flash lamp being adapted to produce flashes of ultraviolet rays, having a com-ponent of a wave length equal to 197.4 nm effective for curing said material and lying within the resonant range of the radical of said material to be cured.

An apparatus as defined in claim 7, in which said ignition unit comprises a source of direct current connected to said flash lamp, a condenser between said source and said flash lamp and connected in parallel to said flash lamp, and an ignition circuit operatively associated with said flash 115

lamp.

An apparatus as defined in claim 8, in which said flash lamp consists of a xenon-filled tube having an ignition winding forming a part of said ignition circuit, said 120 tube at least partly consisting of a material permeable for said rays of said wave length required for initiating said exothermic reaction of said coating material.

10. An apparatus as defined in claim 125 7, further comprising means for supplying a current to said flash lamp having a current density of more than 4000 A/cm² at an output of less than 100 watt seconds and producing said flash so as to last for a 130

**POOR QUALITY** 

period of less than 50 microseconds.

11. An apparatus for carring and hardening a coating applied in a liquid condition substantially as hereinbefore described with reference to the accompanying drawings.

12. A method of carring and hardening a coating applied in a liquid condition substantially as hereinbefore described with reference to the accompanying drawings.

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1345905 COMPLETE SPECIFICATION

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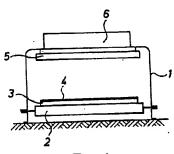


Fig. 1

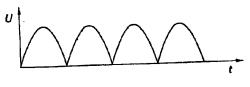


Fig. 2



Fig. 3

COMPLETE SPECIFICATION 134: 305 2 SHEETS This drawing is a reproduction of the Original on a reduced scale Sheet 2

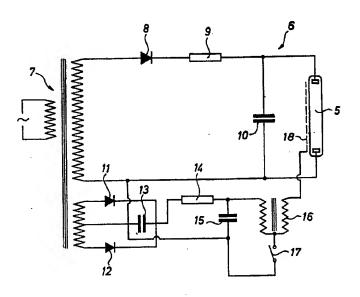


Fig. 4